Patent Application of

Stephen G. Bales

for

TITLE: Lignoellulosic, Borate Filled, Thermoplastic Composites

CROSS-REFERENCE TO RELATED APPLICATIONS: 60/427,113-filing 11/18/2002

FEDERALLY SPONSORED RESEARCH: None

SEQUENCE LISTING: None

BACKGROUND:

[0001] This invention relates to lignocellulosic composites, and more particularly, to lignocellulosic, borate filled, thermoplastic composites.

[0002] There is a very high demand for wood products. Although wood is a renewable resource, it takes many years for trees to mature. Consequently, the supply of wood suitable for use in construction is decreasing and there is a need to develop alternatives.

[0003] Lignoelluosic materials, such as wood, sawdust, rice hulls, and the like have long been added to thermoplastic resins such as polyethylene, polypropylene and polyvinyl chlorine (PVC) to achieve a wood-like composite providing reinforcement, reduced coefficient of expansion, and cost reduction. Process methods have been developed to enable blends containing materials having low bulk density (ie. powders) and poor flow characteristics to be fed at commercially acceptable rates. Blends of this type can be extruded through dies of appropriate configuration to produce building product type

shapes previously made from wood. When these thermoplastic composites were first introduced, the prevailing theory was that the plastic protected the cellulose from fungal attack. However research by Verhey, Laks, and Richer, described in "Laboratory Decay Resistance of Woodfiber/Thermoplastic Composites", Forest Products Journal, September 2001 revealed that lignocellulosic thermoplastics are susceptible to damage from fungal decay. Degradation due to the fungal attack is a problem that threatens the material's structural integrity. In contrast, surface discoloration and spotting has been reported shortly after the introduction of thermoplastic composites. This visual degradation, caused by mold, is a significant problem since major commercial uses of lignocellulosic thermoplastic composites, including decking and fencing, rely on their aesthetic appeal to compete in the marketplace.

[0004] Traditionally, solid wood products are dipped or pressure treated with solutions of fungicides to provide resistance to fungus and mold damage. While this type of treatment is not practicable for a thermoplastic product, it is possible to incorporate a fungicide into the product during its manufacture. This approach provides a constant loading of fungicide throughout the material's thickness, increasing the resistance to leaching of the fungicide from the composite. However it diminishes surface concentration of the fungicide, reducing its effectiveness against surface mold attack.

Anhydrous borate and zinc borate have been used successfully to provide fungal decay at relatively low levels, typically less than 1.5 percent, in lignocellulosic compounds formed from small fractions of wood bonded with an adhesive binder of phenol-formaldehyde resin as described in US Patent 4,879,083. Zinc borate has also been described in the literature as providing resistance to fungal decay in lignocellulosic filled thermoplastics. Research on zinc borate's use as an anti-fungal additive in lignocellulosic thermoplastics has focused on the minimum loading required to increase resistance to fungal decay, while neglecting to consider or investigate the effect of those higher loading levels required to provide resistance to visual deterioration caused by surface molds.

[0005] Although not used commercially as a fungicide, calcium borate is described in US Patent No 6,368,529 and Patent Application No 20020182431 as providing protection against fungal decay and insects in lignocellulosic compounds formed from small fractions of wood bonded with an adhesive binders of phenol-formaldehyde, phenol-resorcinol-formaldehyde, urea-formaldehyde, and diphenylmethanediisocyanate at preferred levels of 1.5% to 15%. All investigation done on the use of calcium borate as a fungicide has focused on its ability to resist fungal decay in lignocellulosic composites such as particleboard, waferboard, oriented strandboard, and medium density fiberboard that use these thermosetting resins.

[0006] The use of calcium borate as a fungicide to increase resistance to fungal decay in lignocellulosic thermoplastics is identified in patent application 20030071389 but has not been studied. The use of calcium borate to increase resistance to surface discoloration caused by surface mold has never been identified or studied, either in lignocellousic composites, which use adhesive binders such as formaldehyde- isocynate-based resins, and or lignocellousic thermoplastic composites using resins including polyethylene, polyethylene, and polyvinyl chloride.

[0007] Currently the lignocellousic thermoplastics industry is faced with two preservation needs: (1) finding an economic method of improving resistance to fungal decay and (2) developing an economic method for improving resistance to the visual damage caused by surface mold.

SUMMARY AND OBJECTIVES OF THE INVENTION

[0008] The present invention, which addresses the above needs, is the incorporation of borates to improve the durability of lignocellulosic thermoplastic products. More specifically it relates to the use of boron-containing fungicides as a preservative to economically increase the resistance of lignocellulosic thermoplastic products to structural decay caused by fungus and to increase the resistance to the visual impairment of the product's surface caused by mold.

[0009] It is an object of the invention is to provide an economic, environmentally safe method of increasing the resistance of a lignocelloulsic thermoplastic to fungal decay.

This is accomplished by the introduction of economic, low toxicity borate materials including calcium borate and boric acid.

[0010] It is a further objective of the invention is to provide an economic, environmentally safe method whereby the lignocellousic thermoplastic has an increased resistance to surface discoloration and other visual impairments caused by mold. It was discovered this can only be accomplished by increasing the borate loading above the 2 percent level by weight. The invention utilizes the robust nature of the thermoplastic binders to accommodate these increased loadings without creating strength or dimensional problems and resulted in the unexpected discovery that borate loading levels as low as 3 percent can provide a significantly increased resistance to surface mold.

DETAILED DESCRIPTION

[0011] The lignocellulosic thermoplastic composites of this invention are produced by well known procedures that combine molten plastic with lignocellulosic fiber and additional additives such as lubricants, process aids, cross-linking agents, inhibitors, stabilizers, blowing agents, foaming agents and other additives known in the art. Examples of suitable thermoplastics include polyethylene (PE), high density polyethylene (HDPE), polystyrene (PS), and polyvinyl chloride (PVC) with loadings by weight from 25% to 75%. This process is further described in U.S. Patent No. 5,516,472 (May, 1996). Examples of suitable cellulosic material include wood, ground rice hulls, kenaf, jute, and coconut shells.

[0012] The methods for manufacturing cellulosic filled thermoplastic are well known and the specific procedure will be dependent on the cellulosic raw material, the plastic, and the type of cellulosic thermoplastic composite desired. However, in general the raw materials are mixed together in a compounding process and the compounded material is then formed into the desired product. Compounding is the feeding and dispersing of fillers and additives, including the fungicide which is in powder form, into the molten polymer using either batch or continuous mixers. The compounded material then is either immediately pressed into the end product or formed into pellets for future processing.

[0013] As used in this invention, the term "boron-containing fungicide" includes calcium borate and boric acid. The calcium borate which can be used in the method of this invention may be any of the borate compounds containing calcium, boron, and oxygen. The calcium borates include the calcium polytriborates, with a CaO:B.sub2 O.sub3 ratio of 2:3 and the calcium hexaborates with a CaO:Bsub2 O.sub.3 ratio of 1:3. Calcium hexaborates include nobleite and gowerite. Optionally, calcium-sodium borates and calcium-magnesium borates may be used; examples include ulexite, probertite and hydroboracite.

[0014] The preferred boron-containing fungicide for this invention are the calcium polytriborates, which may be synthetically produced or a naturally occurring borate such as colemanite or inyonite.

[0015] The exact particle size of the boron-containing fungicide is not critical, but the material must be of a size that can be dispersed uniformly throughout the lignocellulosic thermoplastic composite. Generally a mean particle size as large as 150 microns and as small as 1 micron can be used. For best results the mean particle size should be in the range of 40 microns to 5 microns.

[0016] The amount of boron-containing fungicide incorporated into the lignocellulosic thermoplastic composite will depend on the lignocellulosic content, the longevity desired and the anticipated exposure to moisture. In general, when resistance to decay caused by fungus is required, a range of about 0.2 to 5 percent by weight of the fungicide is required. The preferred amount is about 0.3 to 2 percent for lignocellulosic loadings less than 60 percent and about 2 to 4 percent for lignocellulosic loadings greater than 60 percent.

[0017] When resistance to visual impairment to the surface caused by mold is required, the amount will be in the range of about 2 to 12 percent. The preferred amount is about 3 to 5 percent.

EXAMPLES

Example 1

Lignocellulosic thermoplastic material was produced using a Brabender Conical Twin Screw Extruder with a counter rotating venting screws and forced through a spring die

into test samples 40 cm by 5 cm by 0.2 cm. Prior to extrusion the test samples were blended on a Littleford W-10 mixer as identical mixtures of High Density Polyethylene (HDPE) (>25%), Wood (>40%), Talc (>5%) and Mica (>1%) but with Colemanite loadings of 1, 2, 3, 4, and 5 percent by weight. A sample containing no Colemanite was produced as the control. The Colemanite grade was 47.5 % B.sub.2 O.sub.3, the HDPE was a BP Solvay virgin reactor flake, and the wood was oak.

The five test samples and the control sample were placed in an outdoor exposure for eighteen (18) months. Visual observations and color recordings using with a Macbeth Color-Eye 7000A spectrophotometer were taken at 6, 12, and 18 months (see Table I). When , after 18 months, the six samples were placed next to one another in ascending order by the level of colemanite content a visible improvement was evident as the level of colemanite increased. The control sample had darkened in appearance considerably more that the colemanite containing samples as can be confirmed by the color data shown in Table 1. The samples containing 3, 4, and 5 percent colemanite are all relatively similar in color and obtained the best visual appearance of the six sample set.

As the results show, this calcium borate based material can improve resistance to visual impairment caused by surface mold.

Table 1

Sample	L	a	b	ΔL	Δa	Δb	ΔE
Control							
Initial	64.713	2.266	10.328				
6 month	68.443	0.172	2.879	3.730	-2.095	-7.431	8.574
12 month	64.438	-0.009	1.951	-0.275	-2.276	-8.377	8.685
18 month	63.158	0.007	1.944	-1.555	-2.260	-8.384	8.821
Colemanite 1 %							
Initial	64.968	2.558	10.493				
6 month	69.138	0.181	2.836	4.170	-2.378	-7.657	9.037
12 month	65.673	0.033	2.286	0.705	-2.525	-8.207	8.616
18 month	64.609	0.033	2.406	-0.359	-2.525	-8.087	8.480
Colemanite 2 %							
Initial	65.675	2.382	10.059				
6 month	69.278	0.217	2.903	3.603	-2.165	-7.156	8.299
12 month	67.195	-0.031	2.154	1.519	-2.413	-7.905	8.404
18 month	65.348	0.050	2.469	-0.327	-2.332	-7.590	7.947

Sample	L	a	b	ΔL	Δa	Δb	ΔE
Colemanite 3 %							
Initial	66.452	2.298	9.921				
6 month	69.884	0.171	2.923	3.392	-2.127	-6.998	8.062
12 month	68.417	-0.021	2.331	1.965	-2.319	-7.590	8.176
18 month	66.678	0.057	2.797	0.226	-2.241	-7.124	7.471
Colemanite 4 %							
Initial	65.957	2.307	9.824				
6 month	68.272	0.195	3.102	2.315	-2.112	-6.722	7.417
12 month	68.208	0.020	2.572	2.251	-2.286	-7.253	7.930
18 month	66.048	0.115	3.075	0.091	-2.192	-6.749	7.097
Colemanite 5 %							
Initial	66.106	2.353	10.087				
6 month	69.661	0.187	3.010	3.554	-2.166	-7.077	8.210
12 month	67.495	0.000	2.514	1.388	-2.352	-7.572	8.050
18 month	66.964	0.066	2.914	0.857	-2.286	-7.173	7.277

Lignocellulosic thermoplastic material was produced using a Brabender Conical Twin Screw Extruder with a counter rotating venting screws and forced through a spring die into test samples 40 cm by 5 cm by 0.2 cm. Prior to extrusion two sets of samples were blended on a Littleford W-10 mixer; set 1 contained Wood (70%), High Density Polyethylene (HDPE) (<30%), Talc (>5%) and Mica (>1%) while set 2 was identical but with the addition of a 2 percent Colemanite loading by weight. The Colemanite grade was 47.5 % B.sub.2 O.sub.3, the HDPE was a BP Solvay virgin reactor flake, and the wood was oak.

The samples were sanded and trimmed to 3.2 cm by 2 cm by 0.2cm. Labeled samples were supported on plastic mesh in the bottom of beakers to allow water circulation completely around the samples, covered with 250mL of distilled water, and soaked continuously for 14 days at ambient pressure and temperature. The test specimens were then dried at 40°C to dry for 7 days. Then, the test specimens were placed in a 27 °C, 90% humidity environment for 20 days prior to soil block testing.

The soil block test was conducted in accordance with the American Wood-Preservers Association (AWPA) standard procedure E10-91 with the exception that the brown rot samples were placed in jars at the time of inoculation. The white rot fungus *Trametes* versicolor and the brown rot fungus *Gloeophyllum trabeun* were used for the test. Solid wood controls were paper birch and southern yellow pine (SYP) for the white and brown rot tests, respectively as a test of fungal vigor. The following results were obtained:

Table 2a

SOIL BLOCK TEST RESULTS

White Rot test (*Gloephyllum trabeum)*

Sample Group	Sample #	Weight Loss%	Average %	Std Deviation %
Untreated				
Birch Control	B-1	67.1		
	B-2	63.9		
	B-3	66.9		
	B-4	66.9		
	B-5	65.1	66.0	1.4
Sample Set 1				
No preservative	1-1	33.1		
	1-2	39.6		
	1-3	40.4		
	1-4	26.0		
	1-5	37.8	35.4	6.0
Sample Set 2				
2% Colemanite	2-1	5.1		
	2-2	4.7		
	2-3	2.2		
	2-4	4.8		
	2-5	2.7	3.9	1.4

Table 2b

Brown Rot test (*Gloephyllum trabeum)*

Sample Group	Sample #	Weight Loss%	Average %	Std Deviation %
Untreated SYP Control	P-1	62.0		
	P-2	48.6		
	P-3	50.7		
	P-4	43.0		
	P-5	40.8	49.0	8.3
Sample Set 1 No preservative	1-6	38.6		
	1-7	35.2		
	1-8	36.5		
	1-9	38.1		
	1-10	41.7	38.0	2.5
Sample Set 2 2% Colemanite	2-6	11.2		
	2-7	11.8		
	2-8	3.0		
	2-9	9.4		
	2-10	9.6	9.0	3.5

As the above results show, this calcium borate based additive was effective at controlling *Trametes* versicolor and *Gloeophyllum trabeum*. And, as discovered above, at even this relatively low loading the additive would improve resistance to surface discoloration caused by mold.